

**INVESTIGATING CO<sub>2</sub> RESERVOIRS AT GALE CRATER AND EVIDENCE FOR A DENSE EARLY ATMOSPHERE.** P. B. Niles<sup>1</sup>, P. D. Archer<sup>2</sup>, E. Heil<sup>3</sup>, J. Eigenbrode<sup>4</sup>, A. McAdam<sup>4</sup>, B. Sutter<sup>2</sup>, H. Franz<sup>4</sup>, R. Navarro-Gonzalez<sup>5</sup>, D. Ming<sup>1</sup>, P. Mahaffy<sup>4</sup>, F. J. Martin-Torres<sup>5,7</sup>, and M. Zorzano<sup>6</sup>; <sup>1</sup>Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058; ([paul.b.niles@nasa.gov](mailto:paul.b.niles@nasa.gov)); <sup>2</sup>Jacobs, NASA Johnson Space Center, Houston, TX 77058; <sup>3</sup>HX5-Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, <sup>4</sup>NASA Goddard Space Flight Center, Greenbelt, MD, <sup>5</sup>Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Grenada, Spain, <sup>6</sup>Centro de Astrobiología (INTA-CSIC), Madrid, Spain, <sup>7</sup>Division of Space Technology Department of Computer Science, Electrical and Space Engineering, Lulea University of Technology, Kiruna, Sweden.

**Introduction:** One of the most compelling features of the Gale landing site is its age. Based on crater counts, the formation of Gale crater is dated to be near the beginning of the Hesperian near the pivotal Hesperian/Noachian transition [1, 2]. This is a time period on Mars that is linked to increased fluvial activity through valley network formation and also marks a transition from higher erosion rates/clay mineral formation to lower erosion rates with mineralogies dominated by sulfate minerals [3].

Results from the Curiosity mission have shown extensive evidence for fluvial activity within the crater suggesting that sediments on the floor of the crater and even sediments making up Mt. Sharp itself were the result of longstanding activity of liquid water [4].

Warm/wet conditions on early Mars are likely due to a thicker atmosphere and increased abundance of greenhouse gases including the main component of the atmosphere, CO<sub>2</sub> [5]. Carbon dioxide is minor component of the Earth's atmosphere yet plays a major role in surface water chemistry, weathering, and formation of secondary minerals. An ancient martian atmosphere was likely dominated by CO<sub>2</sub> and any waters in equilibrium with this atmosphere would have different chemical characteristics .

Studies have noted that high partial pressures of CO<sub>2</sub> would result in increased carbonic acid formation and lowering of the pH so that carbonate minerals are not stable [6]. However, if there were a dense CO<sub>2</sub> atmosphere present at the Hesperian/Noachian transition, it would have to be stored in a carbon reservoir on the surface or lost to space. The Mt. Sharp sediments are potentially one of the best places on Mars to investigate these CO<sub>2</sub> reservoirs as they are proposed to have formed in the early Hesperian, from an alkaline lake, and record the transition to an aeolian dominated regime near the top of the sequence [1].

This study seeks to better understand the CO<sub>2</sub> content of the soils and sediments investigated by the MSL rover at Gale crater with the goal of trying to piece together the nature of the atmosphere and climate during the early Hesperian.

**Methods:** The SAM instrument on the MSL rover provides the capability of analyzing drilled sample powders via pyrolysis and evolved gas analysis (EGA) via mass spectrometry [7]. This capability provides an excellent insight into the nature of CO<sub>2</sub> in the samples as the temperature at which CO<sub>2</sub> evolves is highly indicative of the nature of the phase in which it is stored. In general carbonate minerals evolve between 500 and 800 C while reduced carbon phases evolve at temperatures lower than 400 C. In both cases there can be exceptions to this relationship, so it is important to interpret EGA results with care.

**Results:** The SAM instrument has examined 5 different samples from the Gale crater region and CO<sub>2</sub> has been a major volatile component of each sample, however the carbon contents have not indicated that a carbon containing phase such as carbonate minerals make up a significant portion of the samples. All samples have CO<sub>2</sub> contents below 1 wt% but not below 0.1 wt% (Table 1).

The Rocknest soils are the only samples which show a substantial CO<sub>2</sub> evolution above 500° C, indicating the possible presence of carbonate minerals. All of the other samples analyzed to date have shown lower temperature CO<sub>2</sub> releases indicating that the CO<sub>2</sub> is not evolving from a carbonate mineral (see discussion below).

**Discussion:** The presence of significant CO<sub>2</sub> (> 0.1 wt%) within all of the samples analyzed to date suggests that these samples do show some interaction with the atmosphere. However, the amount of CO<sub>2</sub> present and the temperatures at which it evolves are substantially different from what was expected.

The total amount of CO<sub>2</sub> in these sediments does not indicate the presence of a substantial reservoir of CO<sub>2</sub> (Table 1). Assuming that these samples may have similar carbon content to the average martian soil, then a 50 m global equivalent layer (GEL) yields only 50 mbar of CO<sub>2</sub> storage. This is well short of the ~1 bar estimates of the ancient martian atmosphere [5].

The CO<sub>2</sub> releases in all of the samples analyzed to date are also well below 500° C. While it might be possible that this is from a fine grained carbonate mineral [8], this has not yet been demonstrated and most carbonates decompose above 500° C, even Fe/Mg rich varieties.

CO<sub>2</sub> releases are often associated with oxygen releases in the martian data (Fig. 2) suggesting possible combustion of organic matter [9]. However, if this is true it suggests substantial quantities of organic carbon (up to 2000 ppm) (Table 1), and GC-MS analyses do not detect substantial organic fragments that might be associated with kerogen or other complex organic carbon species [10]. Instead it is evolved entirely as CO<sub>2</sub> and CO. This suggests some other form of oxidized carbon may be the carbon source.

One intriguing possibility is Fe(II) oxalate (Fig 1-2) which releases CO<sub>2</sub> at a very similar temperature [10, 11]. Oxalate minerals could form as a result of the breakdown of more complex organic species [11], or could possibly be the result of radiolysis of CO<sub>2</sub> hydrates [12].

**Conclusions:** The total amount of CO<sub>2</sub> in the Gale crater soils and sediments is significant but lower than expected if a thick atmosphere was present at the Hesperian/Noachian boundary. Likewise, the absence of carbonates suggests that CO<sub>2</sub>-weathering processes similar to those present on Earth were not dominant. Instead it is possible that more exotic CO<sub>2</sub> deposition has occurred driven by atmospheric photochemistry and/or degradation of organic carbon.

Table 1. Average CO<sub>2</sub> evolved from samples analyzed by the SAM instrument.

Sample	Evolved CO <sub>2</sub> (μmol)*	C (ppm)	Wt% CO <sub>2</sub>	GEL 10m	GEL 50 m
Rocknest	9.9 ± 1.9	2640	1.0%	11 mbar	54 mbar
John Klein	6.9 ± 1.8	1840	0.7%	8 mbar	38 mbar
Cumberland	2.7 ± 1.0	720	0.3%	3 mbar	16 mbar
Windjana	9.2 ± 2.3	2453	0.9%	10 mbar	48 mbar
Confidence Hills	4.3 ± 1.5	1147	0.4%	4 mbar	21 mbar

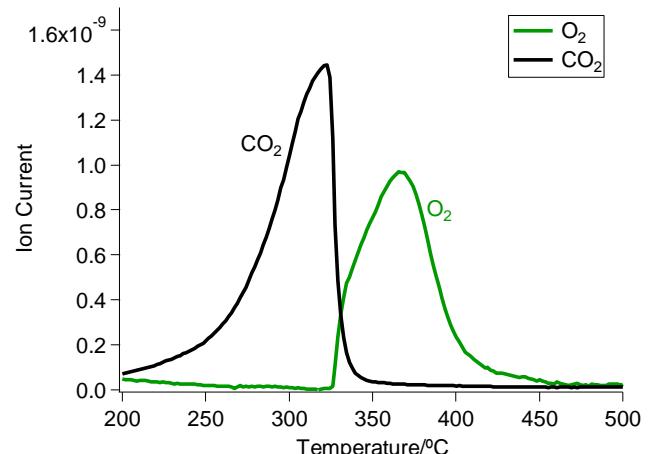


Figure 1. Evolution of CO<sub>2</sub> and O<sub>2</sub> during laboratory analysis of Fe(II) Oxalate + Mg Perchlorate using JSC SAM Testbed [13].

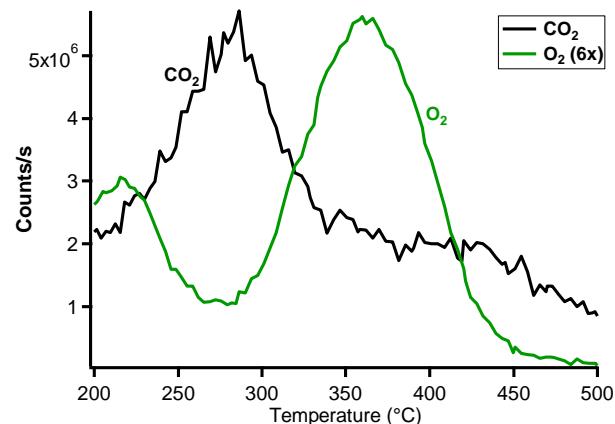


Figure 2. Evolution of CO<sub>2</sub> and O<sub>2</sub> during MSL-SAM analysis of mudstone from John Klein site on Mars.

## References:

1. Milliken R.E., et al. (2010) *Geophysical Research Letters*, 37, 04201.
2. Thomson B.J., et al. (2011) *Icarus*, 214, 413-432.
3. Bibring J.P., et al. (2006) *Science*, 312, 400-404.
4. Grotzinger J.P., et al. (2014) *Science*, 343.
5. Pollack J.B., et al. (1987) *Icarus*, 71, 203-224.
6. Fairén A.G., et al. (2004) *Nature*, 431, 423-426.
7. Mahaffy P., et al. (2012) *Space Science Reviews*, 170, 401-478.
8. Archer P.D., et al. (2014) *LPI Contributions*, 1791, 1075.
9. Ming D.W., et al. (2014) *Science*, 343.
10. Eigenbrode J.L., et al. (2014) *Lunar and Planetary Science Conference*, 45, 1605.
11. Benner S.A., et al. (2000) *Proceedings of the National Academy of Sciences of the United States of America*, 97, 2425-2430.
12. Oshima M., et al. (2012) *Lunar and Planetary Science Conference*, 43, 1976.
13. Leshin L.A., et al. (2013) *Science*, 341.